

PATENT SPECIFICATION

(11) 1 425 822

1 425 822

- (21) Application No. 50222/71 (22) Filed 28 Jan. 1972
 (23) Complete Specification filed 29 Jan. 1973
 (44) Complete Specification published 18 Feb. 1976
 (51) INT CL² C13L 1/08; C08B 15/02, 19/04
 (52) Index at acceptance
 C3U 10E 12B1A2 12B1A6C 12B2J 12B2X 2CX
 C1H 120 620 748 757 785 788
 (72) Inventors GRANVILLE WHITAKER and ARNOLD STANLEY
 FLATAU



BEST AVAILABLE COPY

(54) CEMENTITIOUS COMPOSITIONS

(71) We, FOSROC A.G. (formerly known as Ceimac A.G.), a Swiss Company, of Gartenstrasse 2, 630 Zug, Switzerland, do hereby declare the invention for which we

5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

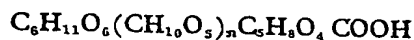
10 This invention relates to cementitious compositions.

According to the present invention there is provided a cementitious composition incorporating a synthetic water-soluble oxidised polysaccharide derivative having an acid value

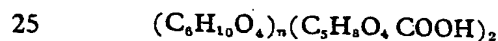
15 of from 10 to 100. The acid value is the amount of KOH in mg which will neutralise 1 gram of the polysaccharide derivative.

20 Preferably the oxidised polysaccharide derivative has an acid value of 30 to 80.

More preferably, the oxidised polysaccharide derivative is of the formula



where n is an integer of from 2 to 32, or of the formula



25 wherein n is an integer of from 6 to 50, preferably from 2 to 20.

It is found that the incorporation of such water-soluble oxidised polysaccharide derivatives in cementitious compositions used in

30 concretes reduces the water requirement for a given concrete workability and enhances the concrete crushing strengths.

The water-soluble oxidised polysaccharide derivatives used in the present invention may be made by selectively oxidising a polysaccharide starting material. Selective oxidising agents which may be used include peroxides, hypochlorites, dichromates, bromine water, peroxy acids, and a mixture of mercuric oxide

40 with calcium carbonate. The reaction may be promoted by heat and tends to be improved if the reaction mixture is alkaline, preferably at a pH from 8 to 14. The solutions formed tend to be acidic and can be used as such

45 or following neutralisation with an alkali metal

hydroxide e.g. caustic soda or caustic potash, or an organic base, e.g. ethylamine or triethanolamine.

Suitable polysaccharide starting materials include starches, thin boiling starch derivatives, pregelatinised derivatives, dextrans, maltodextrins, cellulose and cellulose derivatives.

The cementitious compositions of the invention may comprise other cement additives in addition to the water-soluble oxidised polysaccharide derivative. Thus, cementitious compositions according to the invention may comprise Portland cement, sand and aggregate, together with the water-soluble oxidised polysaccharide derivative.

The following examples will serve to illustrate the invention:

EXAMPLE I.

120 gms of commercially available maltodextrin of molecular weight about 800 was dissolved in 120 gms water and 40 gms 100 volume hydrogen peroxide, together with 0.4 gms of 10% sodium hydroxide solution. The mixture was then boiled until all the peroxide had been used up, as determined by testing with ferrous sulphate. This took about sixty minutes. The colourless solution which was formed was made up to 400 gms with water and had a specific gravity of about 1.12. The acid value of the oxidised polysaccharide derivative so formed was 25.

EXAMPLES II to IV.

Example. I was repeated using as starting materials starch, dextrin and farina dextrin, each having a mean molecular weight of about 4,000 to 10,000. The reaction time increased with the increase in the mean molecular weight. The water-soluble oxidised polysaccharide derivatives so formed had acid values of 14, 19 and 12 respectively.

EXAMPLES V to VIII.

Evaluations were performed to determine the effect of adding the polymeric materials of Examples I to IV to cement or concrete. In each case products defined below were added at the rate of 0.14 litres/50 kgm to

a cement mix comprising one part Portland cement: 2.4 parts sand: 3.6 parts of 5 to 20 mm gravel aggregate. The ingredients were thoroughly mixed with water. The workability was measured by the compacting factor. Setting times were determined using a penetrometer on mortar sieved from the concrete; initial and final setting times were taken when the resistance to penetration reached 0.5 and 3.5 Newtons/mm² respectively.

The results are shown in the Table below in which:

- Example V: the product of Example I with 10% triethanolamine
 Example VI: the product of Example II
 Example VII: the product of Example III
 Example VIII: the product of Example IV following neutralisation with caustic soda solution.

TABLE

Example	Water/ Cement Ratio	Comp- acting Factor	Crushing Strengths N/mm ²			Setting Times Hrs - Mins	
			24 hrs	7 days	28 days	Initial	Final
Control	0.630	0.895	12.4	34.0	47.7	3.00	4.30
V	0.598	0.887	14.1	38.3	51.3	3.50	5.20
Control	0.630	0.869	13.0	34.9	—	3.15	4.40
VI	0.598	0.874	14.6	39.3	—	3.40	5.10
Control	0.630	0.884	12.4	33.6	43.7	2.20	4.30
VII	0.598	0.866	15.2	39.5	52.8	4.15	5.55
Control	0.630	0.884	13.5	34.0	43.7	2.30	3.45
VIII	0.598	0.899	14.7	40.5	49.0	4.00	5.05

The results of the Table show that the polymeric materials reduce the water requirement of a cement mix and increase the compressive strength of formed concrete.

Examples IX and X.

Wheat starch (140 g) was oxidised with sodium hypochlorite (60 g) in water (200 g) to which caustic soda had been added to adjust the pH to about 8 to 9. The reaction was performed at 20°C and stopped when the oxidising agent was used up. The mix was subjected to chromatographic separation on an ion exchange column to isolate the acidic component which took the form of a slightly green viscous solution (a) of acid

value 26. The method was repeated but using sodium dichromate as the oxidising agent and a viscous liquid "(b)" of acid value 42, coloured dark blue because of the chromium, was recovered. The products were tested for their effect on the compressive strength of concrete by adding a sample at the rate of 90 ml/50 kg cement to a 1:6 mixture of cement/aggregate and using water in a water/cement ratio of about 1:0.62. The compressive strength was tested according to BS 1881. For the purposes of comparison, a neutral polymeric saccharide commercially available in Britain was also tested. The results are shown in the following Table:—

40

45

50

Material	Compressive strength		
	24 hours	7 days	28 days
Control	100	100	100
product (a)	108	112	110
5 product (b)	127	110	113
neutral polysaccharide	113	107	102

The tests were repeated using the product (a) at the rate of 86 ml/50 Kg cement and 4 ml/50 Kg cement of triethanolamine in comparison with the neutral polysaccharide and triethanolamine and the following results were obtained:—

Material	Compressive strength		
	24 hours	7 days	
15 Control	100	100	
product (a)	113	118	
& triethanolamine			
neutral polysaccharide	110	112	
& triethanolamine			

20 WHAT WE CLAIM IS:—

1. A cementitious composition incorporating a synthetic water-soluble oxidised polysaccharide derivative having an acid value of from 10 to 100.
- 25 2. A composition according to claim 1, in which the derivative has an acid value of from 30 to 80.

3. A composition according to claim 1 or 2, in which the derivative is of the formula:



where n is an integer of from 2 to 32, or



wherein n is an integer of from 6 to 50.

4. A composition according to claim 3, in which the oxidised polysaccharide derivative is of the formula



and n is an integer of from 2 to 20.

5. A composition according to any of claims 1 to 4 in which the derivative is present in a cementitious composition comprising Portland cement, sand and aggregate.

6. A cementitious composition substantially as described with reference to the Examples.

Agents for the Applicants,
GALLAFENT & CO.,
Chartered Patent Agents,
8, Staple Inn,
London WC1V 7QH.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

BEST AVAILABLE COPY

THIS PAGE BLANK (USPTO)